# Low-Temperature Oxidation of Carbon Monoxide on Pd(Pt)/CeO<sub>2</sub> Catalysts Prepared from Complex Salts

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Abstract—Catalysts containing cerium oxide as a support and platinum and palladium as active components for the low-temperature oxidation of carbon monoxide were studied. The catalysts were synthesized in accordance with original procedures with the use of palladium and platinum complex salts. Regardless of preparation procedure, the samples prepared with the use of only platinum precursors did not exhibit activity at a low temperature because only metal and oxide (PtO, PtO<sub>2</sub>) nanoparticles were formed on the surface of CeO<sub>2</sub>. Unlike platinum, palladium can be dispersed on the surface of CeO<sub>2</sub> to a maximum extent up to an almost an ionic (atomic) state, and it forms mixed surface phases with cerium oxide. In a mixed palladium—platinum catalyst, the ability of platinum to undergo dispersion under the action of palladium also increased; as a result, a combined surface phase with the formula  $Pd_xPt_yCeO_{2-\delta}$ , which exhibits catalytic activity at low temperatures, was formed.

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## INTRODUCTION

The removal of harmful gases, primarily, carbon monoxide and hydrocarbons, from the atmosphere is a problem of considerable current importance. The catalytic neutralization of harmful substances by complete oxidation can be an efficient way for solving this environmental problem. Catalytic oxidation at low temperatures is most difficult to perform. The lowtemperature oxidation of CO and hydrocarbons is required in the neutralization of exhaust emissions in the cold start process, the purification of indoor atmospheres, the operation of lasers based on CO<sub>2</sub>, and other processes occurring at low temperatures [1]. Heterogeneous metal-oxide systems, in which the metal and the oxide exhibit a synergistic effect, belong to the most promising low-temperature catalysts for CO oxidation. The constituents of these systems are platinum group metals or IB Group metals (Cu, Ag, and Au) in a highly dispersed state supported on transition element oxides [2].

It is well known that highly dispersed palladium or platinum supported on cerium oxide and/or ceriumcontaining compositions exhibit considerable catalytic activity and stability [3, 4]. The results of recent studies on these catalysts [5–7] made it possible to conclude that the synergistic effect of a metal–oxide system is due to the chemical interaction of metal and oxide particles and the formation of new phases on the surface. These new surface phases contain active centers at which low-temperature catalytic oxidation takes place. The Pd/CeO<sub>2</sub> catalysts are superior to  $Pt/CeO_2$  in terms of activity in CO oxidation. This is likely due to different degrees of chemical interactions between the above metals or metal oxides and the surface of cerium oxide. The efficiency of this interaction mainly depends on the degree of dispersion of an active component and the temperature of catalyst calcination. As a rule, an increase in the treatment temperature of catalysts based on noble metals is accompanied by a decrease in the catalyst activity. It is believed that a possible reason for this phenomenon consists in changes in the size of metal particles and the particle-size distribution [8]. Thus, in  $Pd/Al_2O_3$ samples calcined at 350°C, the average Pd particle size was  $2.4 \pm 0.4$  nm and the particle-size distribution had a unimodal character. As the treatment temperature was increased, the distribution became bimodal and the average particle size increased. Bimetallic catalysts whose active component consists of two metals are considered more stable. In particular, Yang et al. [9] studied  $Pd_{1-x}Au_x$ ,  $Pd_{1-x}Cu_x$ ,  $Au_{1-x}Cu_x$ , and  $Au_{1-x}Ag_x$  compositions prepared by the laser evaporation of precursors under controlled conditions followed by the condensation of particles and demonstrated that nanosized bimetallic compositions are promising for use in CO oxidation. The temperature  $(T_{50})$  at which a 50% conversion of CO was reached increased in the order  $Cu_{50}Pd_{50}$  (~120°C) <  $Cu_{12}Pd_{88}$  (~135°C) <  $Cu_{90}Au_{10}$  (~145°C) <  $Pd_{88}Au_{12}$  (~190°C). The activity of bimetallic compositions, including Pd—Pt catalysts with different ratios between the noble metals, can increase upon supporting the metals onto an appropriate carrier.

The activity of supported metals depends on a number of factors including the average particle size, the nature of metal–support interactions, the nature of used precursors, and the preparation procedure. Various oxides or mixed oxide compositions are used as supports. Among them, oxides that possess redox properties, for example, CeO<sub>2</sub>, are the most interesting species. As found previously [10–17], Pd and Pt can interact with CeO<sub>2</sub> to form a Ce<sub>1-x</sub>M<sub>x</sub>O<sub>2- $\delta$ </sub> (M = Pd and Pt) solid solution, which changes the catalytic activity, as compared with that of monometallic catalysts.

The most widespread initial noble metal compounds whose solutions are used for impregnating a support are  $H_2PtCl_6$  [18, 19],  $Pd(NO_3)_2$  [20], and  $Pd(CH_3COO)_2$  [21]. However, the use of a chlorinecontaining precursor of platinum seems unreasonable because chloride ions poison the surface of cerium oxide. The formation of cerium oxo chloride ( $Ce^{3+}OCl$ ) prevents the stabilization of supported metals in an active state; because of this, the activity of such catalysts is low [22]. Methods for the formation of nanosized noble metal particles by the decomposition of Pd-containing precursors of another type, namely,  $Pd(Mes)_2$ , where Mes is mesitylene (1,3,5-trimethylbenzene), in a trioctylphosphine solution or  $Pd(CH_3COO)_2$  in an octylamine solution were developed [8]. The process is performed at 300°C followed by the steps of centrifugation and washing with methanol. The preparation of supported catalysts with the use of coordination compounds as precursors makes it possible to eliminate many disadvantages characteristic of traditional procedures. This area has been intensively developed in our laboratory in recent years [23–25].

In this work, we used isostructural complex salts of Pt(II) and Pd(II)—the tetraammine complex nitrates  $[M(NH_3)_4](NO_3)_2$ , where M = Pd or Pt—as precursor compounds for supporting metals onto  $CeO_2$ . These compounds are readily soluble in water to facilitate the impregnation of a support. Note that a solid solution rather than a mixture of individual complexes is formed on the support surface upon the simultaneous crystallization of Pd and Pt compounds. Thus, platinum and palladium become mixed at an atomic level even at the step of supporting a precursor compound. Upon the thermal decomposition of these solid solutions, bimetallic alloy particles in a high degree of dispersion remain on the surface.

Along with thermal decomposition, we additionally tested a procedure of the reduction of supported complex solid solutions by hydrazine hydrate ( $N_2H_4$  ·  $H_2O$ ) at room temperature. Because hydrazine has a high reduction potential, this reagent is widely used in various methods for the reduction of metals [26]. Examples of the preparation of nanoparticles in binary and monometallic catalytic systems based on noble and other transition metals are well known [27–31]. The described procedure makes it possible to form a metal phase from a supported precursor at a low temperature. The intensity of the surface diffusion of nanoparticles formed under these conditions noticeably decreases to facilitate the retention of the metal phase in a highly dispersed state.

In this work, we purposefully studied the effect of the activation procedure of precursor compounds on the structural and electronic states of Pd and Pt and on the activity of  $Pd(Pt)/CeO_2$  catalysts in the reaction of CO oxidation and compared the mono- and bimetal-lic catalysts. For this purpose, we used a set of physic-ochemical and kinetic techniques (see below).

#### **EXPERIMENTAL**

#### Catalyst Preparation Methods

Cerium dioxide prepared by precipitation from a solution of cerium nitrate with an aqueous ammonia solution at certain pH and temperature followed by filtration and washing the precipitate with distilled water until the absence of nitrates was used as a support. The resulting sample was dried initially in air and then in a drying oven at 110°C for 12–14 h; thereafter, it was calcined in a flow of dried air at 450°C for 4 h. The specific surface area of the support was 113 m<sup>2</sup>/g.

Two procedures were used for supporting an active component.

**Procedure I.** The support was incipient wetness impregnated with a solution of a complex salt with a given concentration followed by drying in air for 24 h. To prepare monometallic catalysts, aqueous solutions of a  $[Pd(NH_3)_4](NO_3)_2$  or  $[Pt(NH_3)_4](NO_3)_2$  complex salt were used. The Pd–Pt binary active component with the molar ratio Pd : Pt = 2 : 1 in the resulting solid solution was supported by impregnating the support with an aqueous solution containing both of the complex salts,  $[Pd(NH_3)_4](NO_3)_2$  and  $[Pt(NH_3)_4](NO_3)_2$ , in a ratio of 1 : 2.

The starting complex salts were prepared by the reactions

$$Pd \xrightarrow{HNO_{3}(conc)} [Pd(H_{2}O)_{2}(NO_{3})_{2}]$$

$$\xrightarrow{NH_{3}(conc)} [Pd(NH_{3})_{4}](NO_{3})_{2},$$

$$[Pt(NH_{3})_{4}]Cl_{2} \xrightarrow{2AgNO_{3}} [Pt(NH_{3})_{4}](NO_{3})_{2}$$

**Procedure II.** The support was impregnated with a complex salt solution as described in procedure I; however, after the step of drying, the sample was reduced with hydrazine hydrate ( $N_2H_4 \cdot H_2O$ ) at room temperature; thereafter, the samples were washed with water on boiling and dried in air at 130–150°C.

Catalyst	Supported metal content		Consumption of $H_2$ , $\mu$ mol/g		$H_2/(Pd+Pt)$	
	wt %	µmol/g	total	at the 53°C peak	total	at the 53°C peak
Pd/CeO <sub>2</sub> -I	0.98	92.1	609.3	—	6.6	—
Pd/CeO <sub>2</sub> -II	0.97	91.2	540.7	99.2	5.9	1.1
Pt/CeO <sub>2</sub> -I	2.03	104.1	899.1	—	8.6	—
Pt/CeO <sub>2</sub> -II	2.95	151.2	443.0	_	2.9	_
PdPt <sub>2</sub> /CeO <sub>2</sub> -I	1.1 + 2.54	103.4 + 130.2	781.7	—	3.3	—
PdPt <sub>2</sub> /CeO <sub>2</sub> -II	0.98 + 2.13	92.1 + 109.2	401.8	_	2.0	_

**Table 1.** Consumption of hydrogen in the course of the temperature-programmed reduction of Pd, Pt, and  $PdPt_2$  catalysts supported on  $CeO_2$  with hydrogen

The resulting samples were thermally treated in a flow of oxygen on heating at a rate of 10 K/min to  $450^{\circ}$ C and kept at this temperature for 0.5 h.

The catalysts prepared in accordance with the above procedures are referred to as  $M/CeO_2$ -X, where M = Pd, Pt, or Pd—Pt and X denotes the procedure of supporting an active component (I or II). Table 1 summarizes the concentrations of Pd (Pt) in the samples.

#### Investigation Techniques

Atomic absorption spectrometry (AAS) was used to determine main component concentrations in the samples [32].

The samples were studied by high-resolution transmission electron microscopy (HRTEM) on a JEM-2010 microscope (JEOL, Japan).

The electronic diffuse reflectance spectra of oxide powders in the UV and visible regions were measured in the spectral range of  $11000-54000 \text{ cm}^{-1}$  in air with no pretreatment using a UV-2501 PC spectrometer from Shimadzu with an IRS-250A diffuse reflectance attachment [33].

The X-ray photoelectron spectra (XPS) of the samples, which were ground in an agate mortar and mechanically pressed into an iridium surface of a holder, were obtained on a KRATOS ES 300 XPS spectrometer from Kratos Analytical (United Kingdom). The  $K_{\alpha}$  line of aluminum (or magnesium) with a photon energy of 1486.6 eV (1253.6 eV) was used as primary radiation. The instrument was calibrated based on the position of the Au 4*f* line (84.0 eV). The U''' line in the Ce 3*d* spectrum was used as a calibration standard, the binding energy of which was taken equal to 916.7 eV.

The specific surface areas of the samples were measured using the thermal desorption of argon [34]; the error of this method was  $\pm 10\%$ .

X-ray diffraction (XRD) analysis was performed on a DRON-SEIFERT-RM4 diffractometer with  $CuK_{\alpha}$ radiation. The crystallite size was determined by measuring the physical broadening of individual diffraction profiles using the Scherrer formula. The concentrations of metal components in the samples were determined from the 111 peak area of the fcc phase  $(2\theta = 39.80^{\circ}-40.15^{\circ})$  with normalization to the 002 peak area of the support (CeO<sub>2</sub>). In the course of the quantitative phase analysis, we considered the ratio between the corundum numbers of platinum and palladium ( $I_{corr}$  (Pt)/ $I_{corr}$  (Pd)) to be 1.49.

The catalytic properties of the synthesized samples were tested using a temperature-programmed reaction (TPR) in an automated system with a flow reactor and mass-spectrometric analysis of a gas mixture. A 0.38 g sample with a particle size of 0.25–0.5 mm and a volume of  $0.25 \text{ cm}^3$  was placed in a stainless steel reactor. A reaction mixture containing 0.2 vol % CO, 1.0 vol %  $O_2$ , and 0.5 vol % Ne (the balance was helium) was supplied at a rate of 1000 cm<sup>3</sup>/min to the initial catalyst cooled to  $-15^{\circ}$ C. The space velocity was 240000 h<sup>-1</sup>. In the reaction mixture, the catalyst was heated from -15 to 450°C at a rate of 10 K/min and then cooled in a flow of helium. In the course of the reaction, the concentrations of CO,  $O_2$ , and  $CO_2$  were determined. The concentrations were measured at a frequency of 0.34 Hz.

The temperature-programmed reduction with hydrogen (TPR-H<sub>2</sub>) was performed in an automated system with a flow reactor and mass-spectrometric analysis of a gas mixture. The initial sample was treated in a flow of a gas mixture containing 20 vol % O<sub>2</sub> in He to remove water and carbonates from the surface. A reaction mixture containing 0.1 vol % H<sub>2</sub> and 0.5 vol % Ne (the balance was helium) was supplied at a rate of 1000 cm<sup>3</sup>/min to the initial catalyst (0.2 g) cooled to  $-15^{\circ}$ C. In the reaction mixture, the catalyst was heated from -15 to  $450^{\circ}$ C at a rate of 10 K/min; thereafter, it was cooled in a flow of helium.

## RESULTS

### HRTEM Data

We failed to detect palladium particles in the electron micrographs of sample  $Pd/CeO_2$ -I (Fig. 1a). Nevertheless, the EDX spectra measured in the same support regions suggest the occurrence of a small



**Fig. 1.** (a) HRTEM image of a CeO<sub>2</sub> particle in sample Pd/CeO<sub>2</sub>-I; (b) EDX spectrum, which suggests the presence of palladium in CeO<sub>2</sub> particles shown in Fig. 1a; (c) micrograph of PtO<sub>x</sub> particle aggregates in catalyst Pt/CeO<sub>2</sub>-I; (d) EDX spectrum of the region marked in Fig. 1c; (e) HRTEM image of the support in catalyst PdPt<sub>2</sub>/CeO<sub>2</sub>-I; and (f) EDX spectrum of support particles shown in Fig. 1e.

amount of Pd (Fig. 1b). The atomic concentrations of palladium calculated from the EDX spectra measured in various support regions were always close to the value specified in the catalyst preparation; this fact suggests a uniform distribution of Pd on cerium dioxide. The micrograph of catalyst Pt/CeO<sub>2</sub>-I exhibited platinum oxide (PtO<sub>x</sub>) particle aggregates of size 100–200 nm (Fig. 1c); in this case, the size of particles that formed these aggregates was 10–30 nm. Note that the aggregates of PtO<sub>x</sub> particles were detected in some

support regions, and they were absent from other regions; this suggests a nonuniform distribution of an active component over the support surface. We failed to detect palladium and platinum particles in the electron micrograph of  $PdPt_2/CeO_2$ -I (Fig. 1e). In this case, the calculation based on Ce L, Pd L, and Pt L lines of the EDX spectrum (Fig. 1f) demonstrated that the atomic ratio between Pd and Pt was close to the specified value. Consequently, both palladium and platinum were uniformly distributed on the support in



**Fig. 2.** (a) HRTEM image of a Pt metal particle in sample  $Pt/CeO_2$ -II; (b) EDX spectrum of the particle shown in Fig. 2a; (c) HRTEM image of a bimetallic particle in catalyst  $PdPt_2/CeO_2$ -II; and (d) EDX spectra of two different particles of sample  $PdPt_2/CeO_2$ -II, which suggest the inhomogeneous composition of alloy particles (the spectra of these particles differed in color intensity).

sample PdPt<sub>2</sub>/CeO<sub>2</sub>-I. Figures 2a and 2b show the HRTEM images of catalyst Pt/CeO<sub>2</sub>-II and the EDX spectrum of the marked region, respectively. It can be seen that platinum in this catalyst occurred as coarse metal particles of sizes from 50 to 200 nm. Coarse metal particles of size 100–300 nm were observed in PdPt<sub>2</sub>/CeO<sub>2</sub>-II. One of these particles is shown in an HRTEM image (Fig. 2c). Figure 2d shows the EDX spectra of two different particles of size about 200 nm normalized to the Pt *M* line. It can be seen that the Pd/Pt ratios in these particles were different; this fact suggests an inhomogeneous composition of alloy particles.

Thus, an analysis of the results of electron-microscopic studies demonstrated that ultrafine palladium particles and coarse aggregates of platinum oxide particles were formed in monometallic catalysts upon supporting the noble metals from complex salts. The combined supporting of palladium and platinum in a certain ratio increased the degree of dispersion of platinum in bimetallic catalysts. Upon reduction with hydrazine, coarse Pd and Pt particles were present on the support surface in monometallic catalysts, whereas Pd—Pt alloy particles with various Pd/Pt ratios occurred in bimetallic catalysts.

## Electronic Diffuse Reflectance Spectroscopic Data

The electronic diffuse reflectance spectrum of a  $CeO_2$  sample (Fig. 3a, curve 1) exhibited two intense absorption bands at 36000 and 29000 cm<sup>-1</sup>, which were attributed to  $Ce^{4+} \leftarrow O^{2-}$  charge transfer (CT) bands and a interband transition in  $CeO_2$ , respectively [35]. An additional absorption band at 22000  $cm^{-1}$ appeared in the spectrum of catalyst Pd/CeO2-I (Fig. 3a, curve 2); this band can be attributed to the d-d transition of Pd<sup>2+</sup> ions in an oxygen environment in  $D_{4h}$  symmetry, which is characteristic of small PdO clusters [36]. Considerable changes were observed in the spectrum of catalyst Pd/CeO<sub>2</sub>-II, which was prepared with the use of hydrazine (Fig. 3a, curve 3). Stronger background absorption in the long-wavelength region was characteristic of reduced cerium oxides, and the appearance of a new broad absorption band in the range of 14500-16000 cm<sup>-1</sup> can be ascribed to a CT band due to the  $Ce^{4+}$   $\leftarrow$   $Ce^{3+}$  intervalent transition [37]. Thus, we can conclude that the treatment of a sample with hydrazine facilitated the reduction of cerium oxide.

In addition to the absorption bands of cerium oxide, the electronic diffuse reflectance spectrum of  $Pt/CeO_2$ -I (Fig. 3b, curve 2) exhibited intense absorption bands at 16500 and 21000 cm<sup>-1</sup>, and the spec-

trum of Pt/CeO<sub>2</sub>-II exhibited an absorption band at 21000 cm<sup>-1</sup> (Fig. 3b, curve 3). According to Lietz et al. [38], the most intense absorption band corresponding to the d-d transitions of Pt(IV) in the bulk oxide PtO<sub>2</sub>. H<sub>2</sub>O was observed at 23500 cm<sup>-1</sup>, and it was shifted to shorter wavelength in the spectrum of the supported oxide PtO<sub>2</sub>. The appearance of intense absorption bands in the low-frequency region, which were ascribed to spin forbidden d-d transitions, is characteristic of Pt(II) compounds, for example, square-planar halide complexes [39]. Thus, based on the results of analysis performed by electronic diffuse reflectance spectroscopy, we can hypothesize that Pt(II) oxide was predominant in samples Pt/CeO<sub>2</sub>-II and Pt/CeO<sub>2</sub>-I.

The spectrum of  $PdPt_2/CeO_2$ -I (Fig. 3c, curve 1) was close to the spectrum of Pt/CeO<sub>2</sub>-I in terms of absorption band positions. It contained broad absorption bands with maximums at 16500, 21000, and  $25000 \text{ cm}^{-1}$  in addition to the absorption bands of cerium dioxide. The electronic diffuse reflectance spectroscopic data suggest that Pt(II) oxide was predominant in the bimetallic sample. Based on the results of analysis performed using this technique, it is difficult to identify the oxidized states of palladium because the spectra of platinum oxide compounds superimposed on the spectra of palladium oxide compounds. In the spectrum of PdPt<sub>2</sub>/CeO<sub>2</sub>-II (Fig. 3c, curve 2), an increase in the background absorption in the long-wavelength region and the appearance of an absorption band in the region of  $14500-16000 \text{ cm}^{-1}$ , which is indicative of the appearance of  $Ce^{3+}$  ions. were observed. Thus, the treatment of both PdPt<sub>2</sub>/CeO<sub>2</sub>-II and Pd/CeO<sub>2</sub>-II with hydrazine facilitated the reduction of the support.

# XPS Data

Figure 4 shows the Pd 3d and Pt 4f XPS spectra of all of the catalysts. It can be seen that, in Pd/CeO<sub>2</sub>-I (Fig. 4a), palladium is mainly in the  $Pd^{2+}$  state with BE(Pd  $3d_{5/2}$ ) = 338.2 eV. This peak cannot be attributed to PdO nanoparticles because BE(Pd  $3d_{5/2}$ ) in the structure of PdO is  $337.0 \pm 0.2 \text{ eV} [40-42]$ . According to published data [10, 12–14, 43, 44], this peak characterizes the ionic state of palladium as a constituent of a phase obtained by the interaction of palladium with the surface of  $CeO_2$ ; the composition of this phase can be formally described as  $Pd_xCe_{1-x}O_{2-\delta}$ . In the Pd 3d spectrum, a peak at BE(Pd  $3d_{5/2}) \approx$ 336.7 eV can also be recognized. This peak was observed previously [43, 44], and it belongs to extremely small palladium clusters consisting of a few atoms, mainly as O-Pd2-O dimers [45]. This high value of BE was due to the participation of oxygen ions from the support surface, which affected the palladium clusters to convert them into an ionized state (the Pd<sup>+</sup> state in the case of dimers).



Fig. 3. Electronic diffuse reflectance spectra of (a) (1)  $CeO_2$ , (2)  $Pd/CeO_2$ -I, and (3)  $Pd/CeO_2$ -II; (b) (1)  $CeO_2$ , (2)  $Pt/CeO_2$ -I, and (3)  $Pt/CeO_2$ -II; and (c) (1)  $PdPt_2/CeO_2$ -I and (2)  $PdPt_2/CeO_2$ -II.

The treatment of a sample with hydrazine was accompanied by a dramatic growth of palladium metal particles in catalyst Pd/CeO<sub>2</sub>-II, which were not detected by XPS (Fig. 4b). It is well known [46] that the signal intensity of the core line in the XPS spectrum of an active component on a support is determined from the formula  $I \sim (C_{ac})/d_{ac}S_{sp}$ , where I is the

(a) (b) (d) (c) 338.2 338.0 Pd 3d Pd 3d 336.7 336.5 345 335 340 335 340 345 335 340 345 335 340 345 73.2 73.0 72.6 Pt 4/ Pt 4f 70.9 70 72 74 76 78 80 70 72 74 76 78 80 74 76 78 78 70 72 80 70 72 74 76 80 Binding energy, eV

**Fig. 4.** The (top) Pd 3*d* and (bottom) Pt 4/XPS spectra of catalysts (a) Pd/CeO<sub>2</sub>-I and Pt/CeO<sub>2</sub>-I; (b) Pd/CeO<sub>2</sub>-II and Pt/CeO<sub>2</sub>-II; and (c) PdPt<sub>2</sub>/CeO<sub>2</sub>-I and PdPt<sub>2</sub>/CeO<sub>2</sub>-II.

signal intensity of the core line that characterizes the active component,  $C_{\rm ac}$  is the concentration of the active component,  $d_{\rm ac}$  is the particle diameter of the active component, and  $S_{\rm sp}$  is the specific surface area of the support.

The observed decrease in the Pd 3d signal intensity in the spectrum of sample Pd/CeO<sub>2</sub>-II can be explained only by a decrease in the degree of dispersion of palladium because all of the other parameters remained unchanged. The decrease in degree of dispersion suggests the agglomeration of palladium with the formation of coarse metal particles, as demonstrated below by HRTEM.

An analysis of the Pt 4*f* spectra of  $Pt/CeO_2$ -I indicated (Fig. 4a) that platinum occurred in a state with

**Table 2.** Ratios between metal atoms and cerium atoms in Pd, Pt, and PdPt<sub>2</sub> catalysts supported on  $CeO_2$  (according to XPS data)

Catalyst	Pd/Ce, at %	Pt/Ce, at %
Pd/CeO <sub>2</sub> -I	1.23	_
Pd/CeO <sub>2</sub> -II	0	_
Pt/CeO <sub>2</sub> -I	_	1.60
Pt/CeO <sub>2</sub> -II	—	2.27
PdPt <sub>2</sub> /CeO <sub>2</sub> -I	1.45	1.60
PdPt <sub>2</sub> /CeO <sub>2</sub> -II	0	0.91

BE(Pt  $4f_{7/2}$ ) = 73.2 eV, which is characteristic of the platinum oxide PtO [40].

Catalyst Pt/CeO<sub>2</sub>-II, which was reduced with hydrazine, exhibited an unusual behavior. Both divalent platinum with BE(Pt  $4f_{7/2}$ ) = 72.7 eV and platinum metal with BE(Pt  $4f_{7/2}$ ) = 70.9 eV occurred on its surface. In addition, an insignificant amount of tetravalent platinum with BE(Pt  $4f_{7/2}$ ) = 74.2 eV was present; this is consistent with electronic diffuse reflectance spectroscopic data. The Pt/Ce ratios in samples Pt/CeO<sub>2</sub>-I and Pt/CeO<sub>2</sub>-II were calculated from the results of XPS analysis (Table 2). This ratio in sample Pt/CeO<sub>2</sub>-I was 1.6% at a Pt content of 2.03 wt %, whereas it was 2.27% in sample Pt/CeO<sub>2</sub>-II at a Pt content of 2.95 wt % or 2.32% as converted to a platinum content of 2.03 wt %. These data suggest the same degree of dispersion of platinum in catalysts Pt/CeO<sub>2</sub>-II II and Pt/CeO<sub>2</sub>-I.

In PdPt<sub>2</sub>/CeO<sub>2</sub>-I (Fig. 4c), BE(Pd  $3d_{5/2}$ ) = 338.0 eV, and this suggests the strong interaction of supported palladium with the support and the formation of an interaction phase Pd<sub>x</sub>Ce<sub>1-x</sub>O<sub>2-\delta</sub>. This conclusion is consistent with HRTEM data because no extended palladium structures were detected on the surface of the above catalyst. Nevertheless, an insignificant portion of palladium occurred as two-dimensional cluster structures (BE(Pd  $3d_{3/2}$ ) = 336.5 eV), which cannot be detected by HRTEM. The state of platinum as a constituent of catalyst PdPt<sub>2</sub>/CeO<sub>2</sub>-I corresponds to bivalent Pt<sup>2+</sup>, and only an insignificant portion of platinum was present as metal particles (BE(Pt  $4f_{7/2}$ ) = 71.0 eV). It is believed that the major

portion of platinum as a constituent of this catalyst occurred as a solid solution rather than PtO particles; this solid solution was present in the subsurface layers of CeO<sub>2</sub> along with palladium cations. The Pt/Ce ratio in catalyst PdPt<sub>2</sub>/CeO<sub>2</sub>-I was somewhat lower (1.6%) than that in Pt/CeO<sub>2</sub>-I (upon converting to platinum content, the Pt/Ce ratio becomes 2.0%). Hence, it follows that the degree of dispersion of platinum somewhat decreased at high metal contents.

The reduction of bimetallic catalyst  $PdPt_2/CeO_2$ -II with hydrazine (Fig. 4d) resulted in the formation of coarse Pd metal particles similarly to that upon the reduction of catalyst Pd/CeO<sub>2</sub>-II. In both cases, the particles were large so that the signal from the Pd 3*d* line was not observed. Platinum is less prone to reduction than palladium, and it remained in an oxidized state as PtO with BE(Pt 4f<sub>7/2</sub>) = 72.6 eV after the action of the reducing agent (N<sub>2</sub>H<sub>4</sub>). In this case, PtO particles are sufficiently large, as evidenced by a low signal intensity of the Pt 4*f* line, a decrease in the Pt/Ce ratio, and HRTEM data, which are given in Fig. 2c.

## XRD Data

According to XRD analysis data, the average crystallite size of the support phase was ~10 nm. The crystal lattice parameters of CeO<sub>2</sub> in the catalyst samples were the same as the parameters of a polycrystalline reference sample (JCPDS, file no. 34-394) within the limits of experimental error ( $\pm 0.002$  Å); this suggests a low concentration of reduced cerium (Ce<sup>3+</sup>).

According to XRD data,  $Pd/CeO_2$ -I did not contain a metal phase, and about 80% platinum in  $Pt/CeO_2$ -I occurred as metal particles with an average crystallite size of 30 nm (Fig. 5a). Only an insignificant amount of a metal phase (5% on a total platinum and palladium basis) was detected in  $PdPt_2/CeO_2$ -I. Thus, we can conclude that the total palladium and the major portion of platinum occurred in an oxidized state. The crystallite size in metal particles was 25 nm. According to Darby and Myles [47], who studied the dependence of the crystal lattice parameters of solid solutions on the composition of these solid solutions in the palladium–platinum system, the composition of the detected metal phase is  $Pd_{0.10}Pt_{0.90}$ .

In the samples of series II, the major portion of an introduced metal occurred in an unoxidized state (Fig. 5b). In Pd/CeO<sub>2</sub>-II, 60% palladium occurred as the constituent of a metal phase. The crystallite size was 16 nm. Platinum in sample Pt/CeO<sub>2</sub>-II almost completely occurred in metal particles with a crystallite size of 22 nm. The lattice parameter of a metal phase in PdPt<sub>2</sub>/CeO<sub>2</sub>-II is 3.908 Å, which corresponds to solid solution Pd<sub>0.35</sub>Pt<sub>0.65</sub> [47]. This phase contained about 50% platinum and palladium. The crystallite size was 18 nm.

Attempts to detect and identify the reflections of platinum and palladium oxide phases did not give positive results. This fact can be explained by the superposition of the most intense reflections of oxide phases and the reflections of the support phase and by the weak intensity of these reflections because of low concentrations of active components. Another possible explanation can consist in the binding of oxidized platinum and palladium in Pd(Pt)<sub>x</sub>Ce<sub>1-x</sub>O<sub>2-\delta</sub> phases.

### $TPR-H_2 Data$

The temperature-programmed reduction of the initial samples with hydrogen was performed at a low concentration of H<sub>2</sub> (0.1 vol %) and a high flow rate of a reaction mixture because the sensitivity of this method is inversely proportional to the concentration of hydrogen in the mixture [48].

According to the experimental results (Fig. 6a), one peak with a maximum at a temperature of about 145°C was observed on the reduction of Pd/CeO<sub>2</sub>-I. The amount of consumed hydrogen was 609 µmol/(g catalyst) (Table 1). In this case, the ratio of the amount of consumed hydrogen to the amount of palladium  $(H_2/Pd)$  was 6.6 in the reduction of Pd/CeO<sub>2</sub>-I. The TPR-H<sub>2</sub> curve of Pt/CeO<sub>2</sub>-I exhibited two peaks (Fig. 6a) with maximums at 150 and 250°C. The amount of consumed hydrogen was 899 µmol/(g catalyst), and the  $H_2/Pt$  ratio was 8.6. As can be seen, the amount of consumed hydrogen was much greater than the stoichiometric amount required for the reduction of PdO,  $PtO_2$ , and  $PtO (H_2/PdO (or PtO) = 1;$  $H_2/PtO_2 = 2$ ). The superstoichiometric consumption of hydrogen suggests the participation of oxygen from cerium dioxide in the reduction [49]. Thus, the peak in the TPR spectrum of catalyst Pd/CeO<sub>2</sub>-I corresponds to the reduction of cerium oxide, and the presence of two peaks in the spectrum of  $Pt/CeO_2$ -I can be explained by the reduction of  $PtO_x$  ( $T_{max} = 150^{\circ}C$ ) and cerium oxide ( $T_{\text{max}} = 250^{\circ}$ C).

Another character of reduction was observed in the study of PdPt<sub>2</sub>/CeO<sub>2</sub>-I (Fig. 6a). The TPR-H<sub>2</sub> spectrum of this sample exhibited only a single peak with a maximum at 125°C. Additionally, a low-temperature shoulder was observed in the main peak and the consumption of hydrogen came into play at a much lower temperature of about 0°C. Thus, the simultaneous presence of palladium and platinum shifted the reduction temperature of cerium oxide to the low-temperature region. The amount of consumed hydrogen was 782 µmol/(g catalyst) at the ratio H<sub>2</sub>/PdPt<sub>2</sub> = 3.3.

The character of reduction of the samples reduced with hydrazine was dramatically different (Fig. 6b). The TPR-H<sub>2</sub> spectrum of Pd/CeO<sub>2</sub>-II exhibited a narrow peak with a maximum at 53°C and a broad peak with a maximum at 170°C. The occurrence of a narrow peak suggests a phase transition of oxide structures to a reduced state under the action of hydrogen. The amount of hydrogen consumed at this peak was 99.2  $\mu$ mol/(g catalyst), which corresponds to H<sub>2</sub>/Pd = 1.1 (Table 1). This suggests that the palladium oxide PdO was reduced in this temperature region. The total



Fig. 5. XRD patterns of catalysts (a)  $Pd/CeO_2$ -I,  $Pt/CeO_2$ -I, and  $PdPt_2/CeO_2$ -I and (b)  $Pd/CeO_2$ -II,  $Pt/CeO_2$ -II, and  $PdPt_2/CeO_2$ -II.

amount of absorbed hydrogen was as high as 540.7  $\mu$ mol/(g catalyst), which corresponds to H<sub>2</sub>/Pd = 5.9. Hence, we can conclude that the oxygen of cerium oxide also participated in the interaction with hydrogen. According to XRD data, only about 60% Pd in the sample occurred as metal particles. Hence, it follows that about 40% palladium was in the oxide state (PdO) and interacted with the support. Because of this, the reduction occurred over a broad temperature range, and a maximum was observed at a sufficiently high temperature of 170°C. In this case, not only oxidized palladium but also the surface of CeO<sub>2</sub> participated in the reduction.

The TPR-H<sub>2</sub> curve of Pt/CeO<sub>2</sub>-II exhibited two peaks with maximums at 32 and 90°C. The total hydrogen consumption was 443.0  $\mu$ mol/(g catalyst), which corresponds to the ratio H<sub>2</sub>/Pt = 2.9. This ratio

is higher than that required for the reduction of  $PtO_2$ and PtO. The occurrence of peaks at a low temperature suggests the reduction of oxidized platinum compounds; this is consistent with XPS data, and an H<sub>2</sub>/Pt ratio higher than the stoichiometrically required one suggests the participation of cerium oxide in the process.

The reduction curve of PdPt<sub>2</sub>/CeO<sub>2</sub>-II exhibited two peaks at 14 and 135°C. In this case,  $H_2/PdPt_2 =$ 2.0. This suggests that Pt oxide particles, which were reduced at 14°C similarly to the reduction that occurred in catalyst Pt/CeO<sub>2</sub>-II, were present in the catalyst along with metal alloy particles, which were detected by physicochemical techniques. In addition, an insignificant portion of palladium strongly interacted with the support and activated oxygen from CeO<sub>2</sub>, as evidenced by the occurrence of high-temper-

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**Fig. 6.** The temperature dependence of hydrogen consumption by catalysts (a)  $Pd/CeO_2-I$ ,  $Pt/CeO_2-I$ , and  $PdPt_2/CeO_2-I$  and (b)  $Pd/CeO_2-II$ ,  $Pt/CeO_2-II$ , and  $PdPt_2/CeO_2-II$  in the course of TPR-H<sub>2</sub> and the temperature dependence of CO conversion on catalysts (c) (*1*)  $Pd/CeO_2-I$ , (*2*)  $Pt/CeO_2-I$ , and (*3*)  $PdPt_2/CeO_2-I$  and (d) (*1*)  $Pd/CeO_2-II$ , (*2*)  $Pt/CeO_2-II$ , and (*3*)  $PdPt_2/CeO_2-I$  and (d) (*1*)  $Pd/CeO_2-II$ , (*2*)  $Pt/CeO_2-II$ , and (*3*)  $PdPt_2/CeO_2-II$  and (d) (*1*)  $Pd/CeO_2-II$ , (*2*)  $Pt/CeO_2-II$ , and (*3*)  $PdPt_2/CeO_2-II$ .

ature peaks in the TPR spectrum and an increased value of  $H_2/(Pd + Pt)$ .

#### Catalytic Properties of the Catalysts in CO Oxidation

In Figs. 6c and 6d and Table 3, it can be seen that the Pd-containing catalysts prepared by procedures I and II exhibited different activities. The activity of catalysts was evaluated from three temperatures at which 10, 50, and 90% CO conversions were reached. They are referred to as  $T_{10}$ ,  $T_{50}$ , and  $T_{90}$ , respectively; the value of  $T_{50}$  was most frequently considered. For catalysts Pd/CeO<sub>2</sub>-I and Pd/CeO<sub>2</sub>-II,  $T_{50} = 42$  and 148°C, respectively. Thus, the treatment with hydrazine dramatically decreased the efficiency of catalyst Pd/CeO<sub>2</sub>. On the contrary, the reduction of Pt-containing catalysts with hydrazine somewhat increased

their efficiency in the reaction of CO oxidation, but this increase was insignificant. Thus, for Pt/CeO<sub>2</sub>-I and Pt/CeO<sub>2</sub>-II,  $T_{50} = 148$  and  $134^{\circ}$ C, respectively.

**Table 3.** Catalytic activity of Pd, Pt, and  $PdPt_2$  catalysts supported on  $CeO_2$  in the reaction of CO oxidation

Catalyst	<i>T</i> <sub>10</sub> , °C	<i>T</i> <sub>50</sub> , °C	<i>T</i> <sub>90</sub> , °C
Pd/CeO <sub>2</sub> -I	9	42	125
Pd/CeO <sub>2</sub> -II	110	148	185
Pt/CeO <sub>2</sub> -I	119	148	161
Pt/CeO <sub>2</sub> -II	68	134	161
PdPt <sub>2</sub> /CeO <sub>2</sub> -I	5	40	110
PdPt <sub>2</sub> /CeO <sub>2</sub> -II	68	134	161

The catalytic properties of bimetallic catalysts depend on preparation procedures. Thus, the low value of  $T_{50} = 40^{\circ}$ C was characteristic of catalyst PdPt<sub>2</sub>/CeO<sub>2</sub>-I. Intermediate reduction with hydrazine dramatically decreased its efficiency, so that  $T_{50}$  increased to 134°C. Thus, reduction with hydrazine impaired the performance characteristics of the Pd-and PdPt<sub>2</sub>-containing catalysts, whereas the efficiency of the Pt-containing sample increased in this case, although it did not reach the efficiency of the low-temperature catalyst.

## DISCUSSION

According to electronic diffuse reflectance spectroscopic and XPS data, palladium in catalyst Pd/CeO<sub>2</sub>-I occurred as small clusters (O-Pd<sub>2</sub>-O dimers) and isolated Pd<sup>2+</sup> ions as the constituents of the interaction phase Pd<sub>x</sub>Ce<sub>1-x</sub>O<sub>2-\delta</sub>. The presence of only a single peak at 145°C and the ratio H<sub>2</sub>/Pd = 6.6 in the TPR-H<sub>2</sub> curve supports the occurrence of chemical interaction between palladium and CeO<sub>2</sub>. Thus, the presence of palladium as Pd<sup>2+</sup> ions as the constituents of the interaction phase Pd<sub>x</sub>Ce<sub>1-x</sub>O<sub>2-\delta</sub> and small clusters is responsible for the high activity of this catalyst in the reaction of CO oxidation at low temperatures.

The state of palladium in catalyst Pd/CeO<sub>2</sub>-II treated with hydrazine was essentially different. HRTEM, electronic diffuse reflectance spectroscopic, and XPS data suggest a decrease in the degree of dispersion of Pd because of the formation of coarse particles. This is consistent with the results of XRD analysis, which suggest the presence of a metal phase with an average crystallite size of 16 nm. However, only 60% palladium occurred as a metal. It is likely that a portion of palladium, which cannot be detected by XRD analysis because of the superposition of the most intense reflections of oxide phases and the support phase, occurred as PdO because the TPR-H<sub>2</sub> curves exhibited a peak with a maximum at 53°C and the ratio  $H_2/Pd = 1.1$ . The appearance of a broad and low-intensity peak with a maximum at 170°C in the TPR-H<sub>2</sub> curves was due to the presence of an insignificant fraction of palladium that strongly interacted with the support. The experimental data allowed us to conclude that the treatment of the catalyst with hydrazine resulted in the formation of coarse Pd<sup>0</sup> and PdO particles and an insignificant amount of Pd<sup>2+</sup> as the constituent of the interaction phase  $Pd_xCe_{1-x}O_{2-\delta}$ . In this case, the activity of coarse palladium particles, which did not interact with the support, was close to the activity of catalyst Pd/Al<sub>2</sub>O<sub>3</sub> [50]. Thus, the reaction occurs by the Langmuir-Hinshelwood mechanism, and the initiation of reaction depends on the heat of CO adsorption on metal particles [51], which is as high as 25–35 kcal/mol [52]; because of this, the oxidation of CO cannot be performed at low temperatures.

In catalyst Pt/CeO<sub>2</sub>-I, PtO<sub>x</sub> platinum oxide particle aggregates of size 100–200 nm were present; in this case, the size of particles in the aggregates was 10-30 nm. These data are consistent with the results obtained by electronic diffuse reflectance spectroscopy, which indicated the presence of Pt(IV) and Pt(II) in an oxygen environment in the sample, and by XPS, which exhibited the presence of a main line characteristic of PtO and an additional line due to  $PtO_2$  in the spectrum of this sample. In this case, from XRD data, it follows that about 80% platinum occurred as metal particles with an average crystallite size of 30 nm. This contradiction can be explained by the fact that coarse particles cannot be detected by electronic diffuse reflectance spectroscopy and XPS, whereas, on the contrary, XRD analysis cannot detect platinum in a highly dispersed state. The TPR-H<sub>2</sub> method demonstrated the presence of highly dispersed platinum species in the catalyst, as evidenced by the high temperature of reduction and the superstoichiometric ratio of consumed hydrogen to Pt (8.6). Consequently, we can conclude that a portion of platinum interacted with cerium oxide to form dispersed cationic species. The presence of these platinum species resulted in the appearance of a small peak in the curve of CO conversion in the region of low temperatures (Fig. 6c, curve 2). In this case, in general, the temperature dependence of the conversion of CO was similar to that observed on catalyst  $Pt/Al_2O_3$  [50]. Its shape depends on the heat of CO adsorption on coarse metal particles.

The HRTEM data indicate that platinum in catalyst Pt/CeO<sub>2</sub>-II occurred as coarse metal particles of sizes from 50 to 200 nm. According to the results of XRD analysis, platinum almost entirely occurred as metal particles with a crystallite size of 22 nm. In this case, both platinum metal particles and the dispersed particles of PtO and PtO<sub>2</sub> were detected by XPS. As noted above, XRD analysis provides information on the occurrence of a platinum metal phase, whereas oxide and dispersed states cannot be detected by this technique. The TPR-H<sub>2</sub> method additionally supported XPS data: the occurrence of reduction peaks at a low temperature suggests the reduction of platinum oxide compounds, whereas the somewhat increased ratio  $H_2/Pt = 2.9$  suggests the participation of oxygen from  $CeO_2$  in the process. In this case, the activity of catalyst Pt/CeO<sub>2</sub>-II, as well as Pt/CeO<sub>2</sub>-I, depended on coarse particles.

The HRTEM technique did not allow us to detect palladium and platinum particles in sample  $PdPt_2/CeO_2$ -I. In this case, an analysis of EDX spectra indicated that Pd and Pt were present in the sample and their atomic ratio was close to a specified value. Consequently, both palladium and platinum in sample  $PdPt_2/CeO_2$ -I are uniformly dispersed on the support. According to electronic diffuse reflectance spectroscopic data, supported platinum was a mixture of Pt(IV) and Pt(II) in an oxygen environment. Only an insignificant amount of a metal phase was detected in this catalyst by XRD analysis. In general, Pd and Pt mainly occurred in an oxidized state. This conclusion was supported by XPS data, which suggest the presence of Pd<sup>2+</sup> as the constituent of the interaction phase  $Pd_xCe_{1-x}O_{2-\delta}$  and in O-Pd<sub>2</sub>-O dimers. The state of platinum corresponds to Pt2+, and only an insignificant portion of platinum occurred as metal clusters. The TPR- $H_2$  spectra also supported this conclusion: the occurrence of a single peak with a maximum at 125°C in them and the superstoichiometric ratio  $H_2/(Pd + Pt) = 3.3$  suggests the presence of the ionic forms of Pd and Pt, which interacted with the support, and the participation of cerium dioxide in reduction. Thus, all of the methods suggest the high degree of dispersion of active components on the support surface and their ionic state. This provides the high activity of catalyst PdPt<sub>2</sub>/CeO<sub>2</sub>-I, as well as Pd/CeO<sub>2</sub>-I, in the course of CO oxidation in the low-temperature region.

According to HRTEM and XRD data, coarse Pd– Pt alloy metal particles of size 100-300 nm with various Pd/Pt ratios occurred in catalyst PdPt<sub>2</sub>/CeO<sub>2</sub>-II. XPS also suggests the formation of the coarse particles of palladium metal and PtO. The presence of coarse PtO particles was supported by the TPR-H<sub>2</sub> method because the reduction spectrum exhibited a peak at 14°C. The appearance of a broad peak at a higher temperature suggests that only an insignificant portion of palladium interacted with the support to activate oxygen in CeO<sub>2</sub>. In general, the activity of this catalyst remained low because it depended on the presence of coarse particles, which do not interact with the support.

The entire set of experimental data suggests that, first, the active catalysts based on CeO<sub>2</sub> for low-temperature oxidation should contain palladium as an active component and the low-temperature process on platinum is impossible. Second, the reduction of catalysts with hydrazine leveled the behaviors of palladium and platinum and coarse metal, bimetallic, or oxide particles, which do not exhibit low-temperature activity, were formed in this case on the support surface. Third, the simple incipient wetness impregnation of the support with the solutions of complex precursor compounds made it possible to obtain very active catalysts containing Pd or Pd-Pt as active components. A characteristic property of systems Pd/CeO<sub>2</sub>-I and PdPt<sub>2</sub>/CeO<sub>2</sub>-I, which possess good catalytic characteristics, is an extremely high degree of metal dispersion with the formation of the ionic states Pd<sup>2+</sup> and Pt<sup>2+</sup>. The coarse metal and oxide particles of palladium and platinum were not formed in these catalysts. Low-temperature activity depends on only the inter-

action of palladium and platinum with the surface of  $CeO_2$  with the formation of a new phase state of catalyst components— $Pd_xCeO_{2-\delta}$  or  $Pd_xPt_vCeO_{2-\delta}$  surface solid solutions. The resulting interaction phases possess two new properties: (1) the oxygen constituent of these phases exhibits much higher activity in the catalytic reaction of CO oxidation than the oxygen of the CeO<sub>2</sub> support or oxide particles of palladium and platinum; (2)  $Pd_n^0$  and  $Pt_n^0$  small metal clusters, where  $n \ge 2$ , are stabilized as the constituents of these surface phases. The former property is responsible for the occurrence of oxidation by the stepwise Mars-van Krevelen mechanism because of the activity of lattice oxygen [53]. The latter property facilitates the activation of adsorbed carbon monoxide with the formation of a weakly bound state, and the presence of small metal clusters decreases the enthalpy of CO adsorption to initiate the reaction at a low temperature.

The formation of both an ionic state of platinum as a constituent of the surface interaction phase and platinum metal clusters occurs only under the action of a palladium precursor supported in the synthesis of samples in accordance of procedure I. If platinum precursors are used without the addition of palladium precursors, platinum as a catalyst constituent cannot form surface phases of this type. Note that the formation of the platinum and CeO<sub>2</sub> interaction phases as  $Pt_xCeO_{2-x}$  was detected previously by Bera and coauthors [10-12] with the use of the solution-combustion method. However, the resulting catalysts were not so active at a low temperature as PdPt<sub>2</sub>/CeO<sub>2</sub>-I. Thus, the above data indicate that palladium interacts with the surface of cerium oxide much stronger than platinum. In the absence of palladium, platinum does not form surface interaction phases; only individual phases of metal and oxide particles, which cannot oxidize CO at a low temperature, are formed. The Pd-Pt allov particles also cannot be active sites for the formation of adsorbed states of CO and oxygen, which participate in low-temperature oxidation.

Thus, in this work, we used complex salts to obtain Pd–Pt–Ce oxide catalysts for the low-temperature oxidation of CO. In the catalysts prepared with the use of only platinum precursors, metal and oxide (PtO, PtO<sub>2</sub>) nanoparticles, which do not possess low-temperature activity, are formed on the surface of CeO<sub>2</sub>. In the mixed palladium–platinum catalyst, under the action of palladium, platinum becomes strongly dispersed to result in the formation of a Pd<sub>x</sub>Pt<sub>y</sub>CeO<sub>2- $\delta$ </sub> combined surface phase, which is responsible for the low-temperature oxidation of CO.

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